

Durham Research Online

Deposited in DRO:

24 November 2014

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Webb, A.J. and Dempsey, S.J. and Bloor, D. and Graham, A. and Laughlin, P. and Lussey, D. and Szablewski, M. and Atkinson, D. (2013) 'A novel screen-printed multi-component nanocomposite ink with a pressure sensitive electrical resistance functionality.', in Nanotechnology (IEEE-NANO), 2013 13th IEEE conference on. , pp. 671-674. Proceedings of IEEE conference on nanotechnology.

Further information on publisher's website:

<http://dx.doi.org/10.1109/NANO.2013.6720832>

Publisher's copyright statement:

© 2014 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full DRO policy](#) for further details.

A Novel Screen-Printed Multi-Component Nanocomposite Ink with A Pressure Sensitive Electrical Resistance Functionality *

Alexander J. Webb, Sarah J. Dempsey, David Bloor, Adam Graham, Paul Laughlin, David Lussey, Marek Szablewski and Del Atkinson

Abstract— Here, a novel functional ink is described that is composed of multiple nanoscale components and exhibits pronounced touch pressure sensitive electrical properties ideal for applications in switching, sensing and touch sensitive surfaces. The ink can be screen-printed and the as-printed ink displays a large and reproducible touch pressure sensitive electrical resistance and, in contrast to some other composite materials, the resistance changes occur down to the smallest applied pressures. Detailed scanning electron microscopy shows the complex nanoscale structure of the composite that is critical for the electrical behavior. Current-voltage measurements, under static compressive loading, show monotonic non-linear behavior at low compression and ohmic behavior at higher loadings.

I. INTRODUCTION

Printed electronics is an important area of commercial and academic activity. Examples of established functional applications include photovoltaics and RFID tags.^{1,2} Another area of significant technological importance is that of printed touch sensitive components where applications include switching and location sensing. A key addition to touch sensitive components is the capacity to discern applied force, this would add a third dimension to the current x-y location functionality of current touch sensitive interfaces. Printable concepts for functional force and position sensing for resistive touch pad technologies have been previously demonstrated, however, they required additional printing and lithographic patterning on top of a resistive layer, in the form of a regular array of structural features, needed to enable the combination force sensing with the location sensing capacity.^{3,4}

Ink-jet and screen-printed composites are available, primarily being applied for conductive tracks and electrodes, chemical sensors and thin film transistors.⁵⁻⁸ This work presents a novel screen-printed composite ink,

with electrical properties highly sensitive to compressive stress.

II. EXPERIMENTAL TECHNIQUES AND METHODS

The ink comprises acicular titanium dioxide needles, typically 1.6 μm by 100 nm, coated with a semi-conducting surface layer of antimony doped tin dioxide, and approximately spherical wide band-gap (essentially electrically insulating) titanium dioxide nanoparticles of mean diameter 200 nm, dispersed in an insulating polymer ink, such as a polyvinyl resin like Polyplast Type PY383.⁹ The spherical nanoparticles have a dispersant surface coating, such as the commercially available Triton X, which aids their dispersion throughout the polymeric base and ensures a uniform distribution between the acicular particles. The conducting acicular and insulating spherical particles are blended in to the polymer ink until a homogeneous suspension is obtained. The ink was printed using a conventional manual load semi-automatic flat bed screen printer, with a 1 μm tolerance. After printing, the ink was dried at 90 $^{\circ}\text{C}$ for 30 minutes.

Test devices were made by printing the ink on to a polyethylene terephthalate (PET) substrate. The devices were constructed by successively printing a conducting silver track and carbon electrode, followed by a layer of the functional ink, on to a lower element of PET. The upper element comprised a silver track and carbon electrode printed on a complimentary PET substrate. The upper electrode was brought into registry with the lower element to form the test device. The device schematic and final appearance are shown in Fig. 1.

The structure of the as-printed ink was studied using a Hitachi SU70 Analytical scanning electron microscope. The devices were used in tests to determine the sensitivity of the inks' electrical resistance to compressive stress. This was undertaken using a Lloyd LRX test station using a Tricor Rubber Tip Model 933A force probe, conforming to ASTM standard F1578 that is intended to replicate the response of finger pressure on the device. The test devices were also

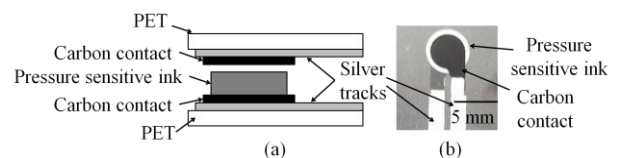


Figure 1. (a) A schematic diagram of the test sensor and (b) a photograph of a complete ink sensor from the top down.

*Research supported by Peratech Ltd and the EPSRC.

Alexander J. Webb, Sarah Dempsey, Marek Szablewski, David Bloor and Del Atkinson are with the University of Durham, Department of Physics, South Road, Durham, DH1 3LE, UK(phone: +44(0) 191 3343529; e-mail: a.j.webb@durham.ac.uk).

Paul Laughlin, David Lussey, Sarah J. Dempsey and David Bloor are also with Peratech Ltd, Old Repeater Station, 851 Gatherley Road, Brompton on Swale, DL10 7JH, UK(phone: +44(0) 1748 813670; e-mail: david.bloor@peratech.com)

Adam Graham was with Peratech Ltd, Old Repeater Station, 851 Gatherley Road, Brompton on Swale, DL10 7JH, UK. He is now with PolyPhotonix, NETPark, Thomas Wright Way, Sedgefield, TS21 3FD, UK (phone: +44(0) 1740 625700; e-mail: info@polyphotonix.com).

subject to current-voltage sweeps at fixed compression using a computer controlled Keithley 2420 and a custom compression rig based on a micrometer mechanism.

The voltage across the test device was varied from 0 V to 10 V at 0.1 V steps over 100 seconds, then decreased to 0 V at the same rate. This whole process was repeated for 10 cycles. Control devices comprising just silver and carbon electrodes on the PET were subject to I-V tests and showed only ohmic behavior and no pressure sensitivity.

III. RESULTS AND DISCUSSION

The inks used in this study were made with filler particle concentration and size optimized for touch and location sensing. The results presented here are representative of all the samples studied.

A. Physical Structure

The structure of the as-printed ink, revealed by high-resolution SEM imaging, is shown in Fig. 2 (a). The acicular particles, while having the tendency to clump into aggregates of a few particles in some places, are widely dispersed across the surface, orientated randomly both on and into the ink surface. The approximately spherical nanoparticles, however, are more uniformly dispersed, and prevent the acicular particles from aligning with one another into a liquid crystal like structure, and likely prevent preferential alignment of the acicular filler during the printing process. Voids present in the ink layer lend to the inks' compressibility. This physical structuring is of great importance for the pressure sensitive conduction mechanisms. Fig. 2 (b) and Fig. (c) show histograms for the dimensions of the acicular filler particles and the diameter of the insulating nanoparticles.

B. Electrical Behavior

The touch pressure sensitivity of the electrical resistance as a function of compressive stress is shown in Fig. 3.

The initial resistance of the ink typically exceeds 10 M Ω . This indicates negligible contact between the ink surface and upper contact until a force is applied. A large decrease in resistance is observed for forces below 0.01 N. This response is likely due to increasing contact between the upper electrode and acicular particles lying out of the plane of the ink surface. By 0.1 N, the resistance has fallen to circa 7.5 k Ω . The rate of decrease with increasing force slows, indicating that intimate contact has been established between the electrode and the ink. This behavior contrasts with that of other composites which are largely insensitive to force below 5 N.^{10,11} The resistance typically drops to circa $10^2 \Omega$ with just 3 N of applied compression. At higher forces, compression of the ink body causes diminution of the void spaces in the ink layer and increasing close contact of the acicular particles. The resistance falls more gradually as the applied force increases. These changes are reflected in the nature of conduction in the device, as discussed below.

As part of the current-voltage analysis of the ink, the test devices were placed under a constant pressure. Some creep behavior was observed, with the resistance settling to a constant value after approximately ten minutes. At low

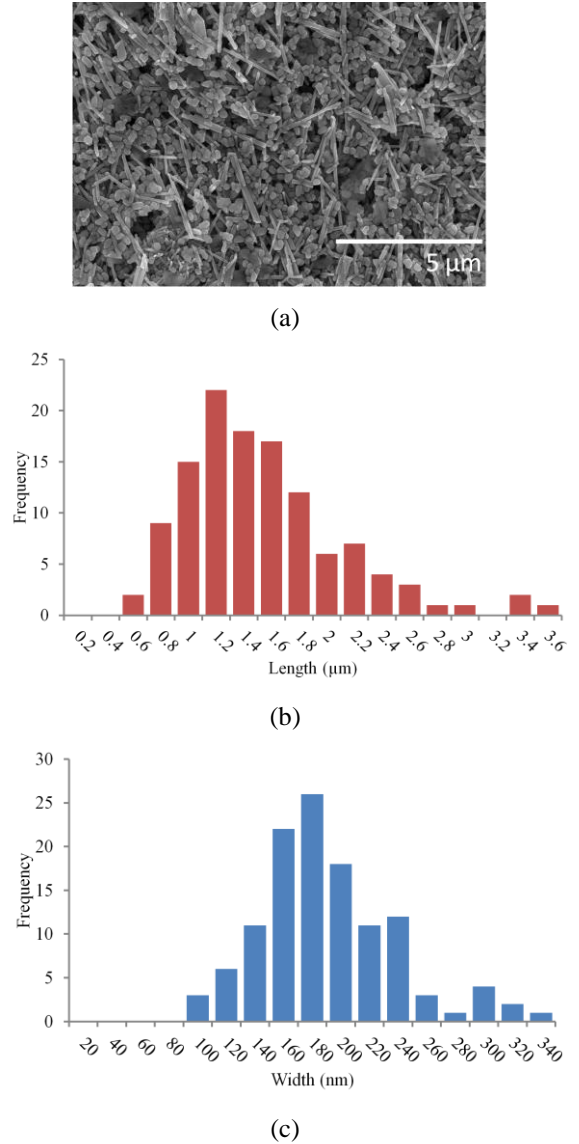


Figure 2. (a) A wide view of the ink surface, showing clumps of acicular semi-conducting particles and approximately spherical insulating nanoparticles dispersed across the surface. Voids in the printed ink are seen across the surface (b) Histogram of acicular particle length (c) Histogram of nanoparticle width.

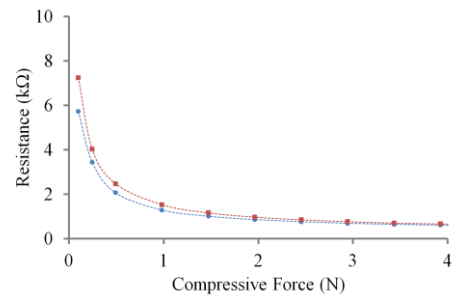


Figure 3. Data showing the relationship between the electrical resistance of the ink and applied force, averaged over 5 tests. Blue circles are data from the first compression to 10 N, red squares are data from after 1 million compressions.

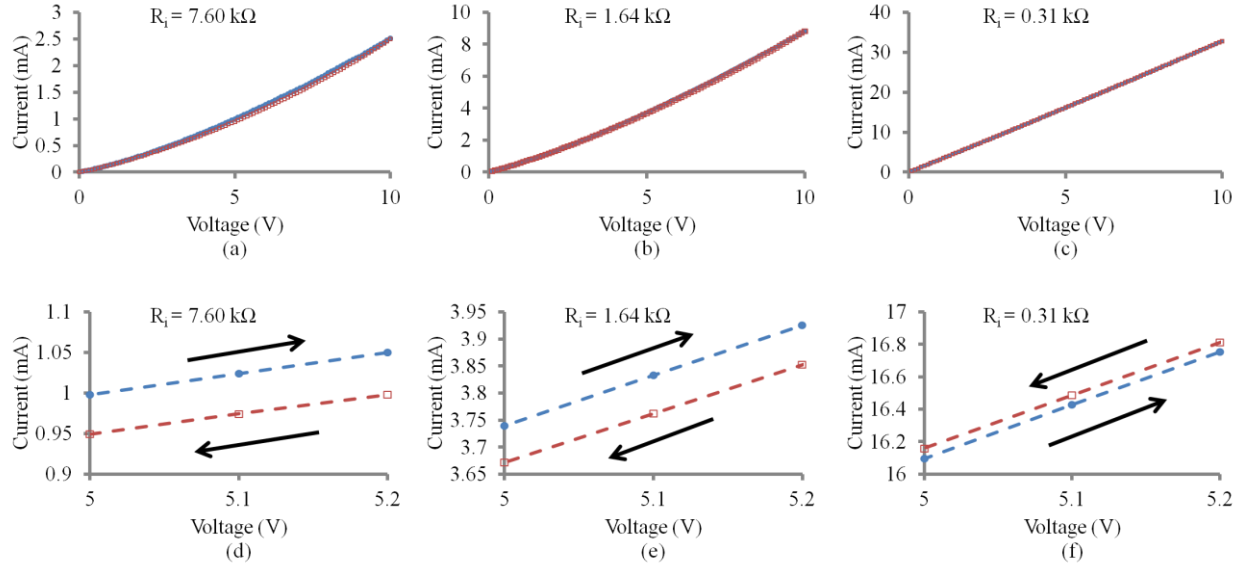


Figure 4. I-V curves taken at (a) low compression, (b) mid compression and (c) high compression. Blue solid circles indicate the ramp up of voltage, red open squares indicate the ramp down. As the compression is increased, the I-V characteristic becomes ohmic. Magnified areas of the I-V curves are shown in (d), (e) and (f). There is a small degree of hysteresis at all compressions, but the hysteresis reverses at the highest compressions. Error bars representing the error on the current measurements are smaller than the data points.

compression, the I-V characteristic is non-linear, with an increasing gradient at higher voltage. This is shown in Fig. 4 (a). At mid compression, Fig. 4 (b), the I-V is still non-linear. In contrast, the I-V is largely linear at high compression, though a very small non-linear contribution remains as shown in Fig. 4 (c). A small degree of hysteresis is observed in the I-V data at both low and high compressions, but is reversed at the highest compressions, shown in Fig. 4 (d), (e) and (f).

Work on composites with non-linear I-V characteristics, by He and Tjong (2011 and 2012), suggest a combination of linear ohmic percolative conduction and quantum tunneling internal field emission conduction mechanisms, given in (1), can describe the observed I-V characteristics well.^{12,13}

$$J(E)_{\text{TOTAL}} = \sigma_0 E + AE^n \exp(-B/E) \quad (1)$$

Where $J(E)_{\text{TOTAL}}$ is the total current density, σ_0 is the linear conductivity (from percolative direct electrical contact between filler particles), A is a parameter related to the tunneling frequency and contains many correction factors, such as the field enhancement factor, E is the electric field, B is a value related to the potential barrier height and n is a constant that varies between 1 and 3, depending on the mode of tunneling, equaling 2 in the special case of Fowler-Nordheim tunneling.

Fitting of the model to the data in Fig. 5 (a) and (b) is good. The residuals in Fig. 5 (c) and (d) show that, while this model does not explain everything, it is certainly a good foundation to build upon in understanding the conduction mechanisms present in the ink. Values for the linear conductivity and parameter A were extracted for analysis with varying compression, shown in Fig. 6 (a) and (b). We see that both undergo a similar increase during initial contact up to 0.1 N force. Between 0.1 N and 1 N force, parameter A

risks dramatically, while the linear conductivity rises at a shallower gradient. Above 1 N, however, we see a quenching of parameter A and a sharp increase in the linear conductivity.

The behavior of the parameters σ_0 and A reflect the processes dominant in conduction through the ink. At 0.1 N, full contact between the ink and the electrode is established. Between 0.1 and 1 N the ink is compressed and the acicular particles get closer together. This increases the number of direct electrical connections, but more significantly increases the efficiency of field assisted tunneling by narrowing of the tunneling barriers. By 1 N, compression has led to a majority of acicular particles being in intimate contact. Above 1 N, direct electrical contacts come to dominate conduction. The contribution of quantum tunneling to charge conduction through the ink is greatly reduced. Hence the ink is driven into a more ohmic conducting state.

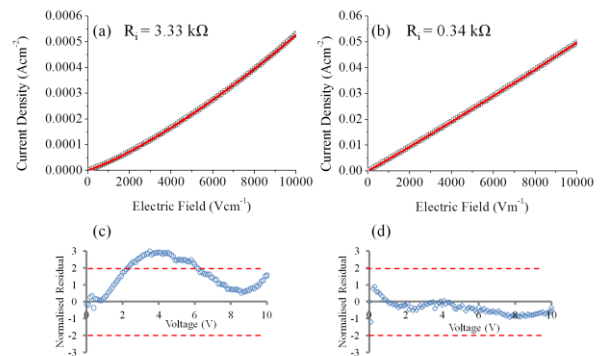


Figure 5. Fits of equation (1) to I-V data taken at (a) lower compression and (b) higher compression. The solid red lines in (a) and (b) are the model fit, the open black squares are the I-V data. Below each fit is a plot of the normalized residuals for (c) low compression and (d). The dashed red guide lines indicate the +/-2 cut off for a good fit.

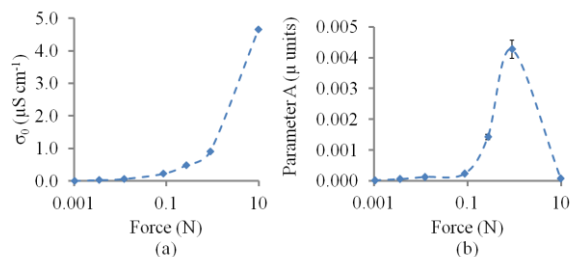


Figure 6. The behavior of (a) the linear conductivity and (b) parameter A in relation to the applied force on a logarithmic scale

IV. CONCLUSION

A functional multi-component, nanocomposite ink has been developed which displays electrical behavior with a very high and reproducible sensitivity to touch pressure. The behavior of electrical resistance in response to compressive stress showed three distinct regions. Below 0.1 N, initial contact between the surface of the ink and the upper electrode is established. Above 0.1 N, the ink undergoes compression and the contribution to charge conduction from direct, percolative connections and field assisted quantum tunneling are increased, but the tunneling dominates. Above 1 N, compression of the ink leads to most of the acicular filler particles being in direct contact. This causes conduction through direct contacts to dominate, quenches quantum tunneling and results in a more ohmic I-V characteristic. It is the combination of semi-conducting, high aspect ratio acicular particles and insulating nanoparticles in an insulating polymer ink, used as a binder to wet the particles, that forms a structure critical for this electrical behavior and high sensitivity. The choice of nanoscale filler particles has enabled this ink to be printed with conventional screen printing technology. The development of this nanocomposite ink presents a unique opportunity for three dimensional touch interfaces for location and force sensing.

ACKNOWLEDGMENT

All authors would like to thank Leon Bowen at the Durham Microscopy Facility.

REFERENCES

- [1] Shrotriya V 2009 "Organic Photovoltaics; Polymer Power" *Nat. Photonics*, **3** 447-499.
- [2] Lakafosis V, Rida A, Vyas R, Yang L, Nikolaou, S and Tentzeris M 2010 "Progress Towards the First Wireless Sensor Networks Consisting of Inkjet-Printed, Paper-Based RFID-Enabled Sensor Tags" *Proc. IEEE*, **98** 1601-1609.
- [3] Chang W-Y, Fang T-H, Shen Y-T and Lin Y-C 2009 "Flexible Electronics Sensors for Tactile Multiscanning" *Rev. Sci. Instrum.* **80** 084701:1-8.
- [4] Kim D-K, Kim J-H, Kwon H-J and Kwon Y-H 2010 "A Touchpad for Force and Location Sensing" *ETRI J.* **32** 722-728.
- [5] Mionić M, Pataky K, Gaal, R, Magrez A, Brugger J and Forró L 2012 "Carbon nanotubes-SU8 Composite for Flexible Conductive Inkjet Printable Applications" *J. Mater. Chem.* **22** 14030-14034.
- [6] Lim S, Kang B, Kwak D, Lee W H, Lim J A and Cho K 2012 "Ink-Jet Printed Reduced Graphene Oxide/Poly(Vinyl Alcohol) Composite Electrodes for Flexible Transparent Organic Field-Effect Transistors" *J. Phys. Chem. C*, **116** 7520-7525.
- [7] Loffredo F, De Girolamo Del Mauro A, Burrasca G, La Ferrara V, Quercia L, Massera E, Di Francia G and Della Sala D 2009 "Ink-Jet Printing Technique in Polymer/Carbon Black Sensing Device Fabrication" *Sensors and Actuators B*, **143** 421-429.
- [8] De Girolamo Del Mauro A, Grimaldi I A, Loffredo F, Massera E, Polichetti T, Villani F and Di Francia G 2010 "Improvement of the Inkjet Printed VOCs Sensor Performances Through The Sensing Layer Geometry" *AIP Conf. Proc.* **1255** 345-347.
- [9] Peratech Ltd., *UK Patent GB 2462920*.
- [10] Qu S and Wong S-C 2007 "Piezoresistive Behaviour of Polymer Reinforced by Extended Graphite" *Comp. Sci. Technol.* **67** 231-237.
- [11] Abyaneh M K and Kulkarni S K 2008 "Giant Piezoresistive Response in Zinc-Polydimethylsiloxane Composites Under Uniaxial Pressure" *J. Phys. D: Appl. Phys.* **41** 135405:1-7.
- [12] He L and Tjong S-C 2011 "Nonlinear Electrical Conduction in Percolating Systems Induced by Internal Field Emission" *Synth. Metals*, **161** 540-543.
- [13] He L and Tjong S-C 2012 "Universality of Zener Tunneling in Carbon/Polymer Composites" *Synth. Metals*, **161** 2647-2650.